The Cretaceous-Tertiary Cataclysm and its Aftermath: Evidence from Two New Zealand Sites

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Abstract. Five K-T boundary sites in Europe and New Zealand are enriched 10^2-10^4-fold in elemental C (mainly soot) and Ir, apparently from major fires following meteorite impact. The carbon abundance corresponds to a global deposit of 0.013 ± 0.007 g/cm^2, i.e. 7% of the total living carbon. The isotopic composition of the K-T carbon is constant at all 5 sites, $\delta^{13}C_{PDB} = -25.4 \pm 0.3$‰. This suggests a single global soot component, either from a single source (fossil C) or from several sources mixed globally before deposition (forests). Charcoal from trees best matches the isotopic composition, but fossil carbon cannot be ruled out. Isotopic data on carbonate and kerogen in the boundary clay show marked fluctuations, suggesting brief, $10°$ warming, respiration by plankton during a period of darkness, and rapid burial by ejecta.

In an earlier paper (1) we reported the presence of soot at three widely separated K-T boundary sites, and suggested that it came from major fires triggered by the impact of a giant meteorite (2,3). Apparently some dramatic environmental changes -- impact, fires, darkness, heat, cold, etc. -- took place in the brief interval represented by the boundary clay. In an attempt to resolve this sequence of events, we have made a detailed study of the K-T site at Woodside Creek, New Zealand (4), whose very sharp Ir profile (5) implies minimal disturbance. Apart from C, we have measured Ir and 32 other elements by RNAA and INAA as well as carbon and oxygen isotopes (6). Our samples were aliquots of the powders used by Brooks et al. (5), of which 15 covered the interval -4.5 to +34 cm continuously, whereas 12 others extended the range discontinuously to -243 and +250 cm. The boundary clay, only 0.6 cm thick at this location, had been subdivided into 3 layers by cuts at 0.3 and 0.4 cm. In addition, we have measured several samples from Chancet Rocks, New Zealand (7,8), Stevns Klint, Denmark, and Nye Kløv, Denmark (6,9).

A major improvement over our previous work was a new procedure for resolving the two principal carbon components, kerogen and elemental carbon, and for subdividing the latter into soot (Fig. 1a) and coarse carbon (Fig. 1b). Earlier authors (10) had concluded that similar coarse carbon in marine sediments is charcoal derived from fires on land. As before, we isolated a carbonaceous residue by dissolving the rock in HF-HCl, but then removed kerogen by etching with $Cr_2O_7^=$ under controlled conditions (11), rather than by NaOH and organic solvents (1). The unetched and etched samples were then combusted to CO_2 for mass spectrometric analysis, yielding isotopic data and weights for elemental C and kerogen (the latter by difference) as well as the content of insoluble minerals. The elemental C was examined on

the SEM and the mass fraction of soot was found by planimetric analysis (12).

Carbon and Iridium Profiles at Boundary. Fig. 2 shows the data for the ~3 m section straddling the boundary, with the -5 to +35 cm and especially the 0 to +0.6 cm intervals expanded. No corrections for carbonate content were made. Iridium and elemental C both rise sharply at the boundary, by factors of 1400 and 210 compared with the Cretaceous average of 0.076 ppb and 22 ppm (13). Both reach their maximum in the basal 0.3 cm of the boundary clay and decline afterwards, but the decline for Ir is greater and more regular. Soot, with a Cretaceous average of <1 ppm, shows an even steeper rise (>7000x) in the basal layer and becomes a major component (up to 71%) of the elemental C in the boundary clay, as shown by the convergence of the two curves. It then declines sharply, rather like the Ir curve but with considerable oscillations, especially at +7.6 cm and +27.6 cm. Above the boundary, soot is only a minor (1 to 29%) component of the elemental carbon. All 3 curves approach Cretaceous levels only at ~250 cm. Let us review the implications of the data.

Carbon Enrichment at the Boundary. The large, abrupt rise in C and Ir at Woodside Creek is not unique. The Chancet Rocks site, 15 km away, shows a similar increase (Fig. 3). Although this site is tectonically disturbed (7) and lacks boundary clay in places (14), it, too, shows a steep rise in elemental C and Ir at the boundary, by factors of 3 x 10^5 and 290, respectively.

The rise in C at Chancet Rocks may have been exaggerated by local geologic factors (15). Still, it is curious that our earlier data for the Danish K-T boundary -- the only place for which we had comparison samples for the Cretaceous and Tertiary -- showed only a fourfold increase in carbon

abundance (1). Two likely reasons are incomplete removal of kerogen and lack of a correction for insoluble minerals (mainly rutile), which would cause our carbon values to be high. We have therefore reanalyzed the Nye Kløv Cretaceous and Tertiary marls, using our new procedure for removal of kerogen. The new elemental carbon value is only slightly lower for the Tertiary sample (830 vs 1040 ppm), but is substantially lower for the Cretaceous sample (240 vs 950 ppm), corresponding to a 15-fold rise in carbon concentration at the boundary. The soot contents are lower still: 19 and 3 ppm, compared to 1930 ppm for the boundary clay. Thus even the Danish samples show a ~600-fold increase in soot concentration at the boundary. Such an increase cannot possibly be due to condensation of the section by dissolution of carbonate, as argued by Officer and Ekdale (16), as this mechanism can raise concentrations only by the ratio of clay contents, i.e., a factor of 7 for the Danish section. But the factors actually required are larger and highly variable: 15 for elemental C, 600 for soot, and 2000 for Ir (this work and 17); the Ir and soot values require that some 600 m or 180 m of >99.8% pure carbonate condense to 30 cm of boundary clay! In a remarkably selective reading of the literature, Hallam (18) has recently repeated the condensation argument of (16), although its absurdity -- and the much greater carbon enrichments at other sites -- were pointed out on the facing page of Science (17).

Prompt or Delayed Fires? Several authors (19) have pointed out that an impact is unlikely to start a global wildfire, as living trees do not burn well. They suggest instead that forests were killed and freeze-dried by the initial darkness and cold following the impact, and were then ignited by lightning after the sky had cleared and thunderstorms had resumed.

According to this model, soot should first appear on top of the Ir-

bearing ejecta, as fires would start only after the ejecta had settled. But Fig. 2 shows that soot accompanied Ir even in the first fallout fraction; both rise more than 200-fold in the bottom 0.3 cm of the boundary clay. Apparently the fire was in progress well before the ejecta had settled. We leave open for now the source of the fuel: biomass or fossil carbon.

Deposition Time of Boundary Clay. No absolute dating method can measure events as short as 10^5 yr, let alone 1 yr, that occurred 65 Myr ago (20). However, there are several constraints on the deposition time of the boundary clay and subsequent fallout.

First, let us check how sharp a time marker the Ir spike represents, using a plot that also includes 3 other elements enriched in boundary clay, all on a carbonate-free basis (Fig. 4). Ir begins to rise at -4.5 cm, but actually Al, Fe, and Sb -- non-meteoritic indicators of boundary clay -- also rise from -4.5 to 0 cm, while the carbonate content drops (Fig. 4). Thus the rise in Ir in this interval apparently represents admixture of ~5% boundary clay, not a premonitory Ir signal. It would seem that the Ir peak at 0 cm is indeed a sharp time marker, representing the sudden injection of $~10^{-7}$ g/cm^2 of Ir or ~0.2 g/cm^2 of meteoritic material [if the Ir is meteoritic, for which there is ample evidence (3,17,21)].

Next, we consider the settling time of the boundary clay. This clay, averaging 2-5 g/cm^2 worldwide, apparently represents impact ejecta that subsequently weathered to smectite clay (22). The original particle size of the ejecta may have been mainly >1 μm, judging from some surviving material in the boundary clay: spherules up to 1000 μm (23) and shocked quartz grains in the 1-100 μm range (24). These ejecta must have fallen out of the atmosphere in less than a year (25), and should have settled through a few

hundred meters of water in a similarly short time. (By Stokes' law, 1 μm grains take 1 year to settle through 100 m of water; as $t \propto r^{-2}$, the time is much shorter for larger grains).

Strong ([4]) has noted that microfossils corresponding to ~10^4 yrs of the Lowest Teurian were not observed in his samples, but notes ([4,26]) that this could be due to sampling rather than to a genuine hiatus. In a private communication ([26]) he explains that his work was only of a preliminary nature and a more detailed examination, in light of the latest knowledge, might have led to the discovery of Lowest Teurian microfossils which have been found -- though in low abundance -- in the nearby Flaxbourne River site ([21]).

Primary and Secondary Fallout. In the Tertiary, Ir and all 3 forms of C remain elevated above Cretaceous levels to at least +34 cm (Figs. 2,3), reverting to normal only above +213 cm at Woodside Creek. A similar trend for Ir alone has been seen at other sites, and is usually interpreted in terms of two kinds of fallout: primary, represented by the boundary clay ([27]) or even only its basal layer ([28]), and secondary, represented by the remaining material of elevated Ir content. The amount of Ir and C in this secondary fallout is much larger than that in the primary fallout (Table 1), especially if the integration is carried to +250 cm (this involves considerable interpolation, as we have only 6 samples between +34 and +250 cm, covering about 9% of the section). The time interval represented by this 250 cm is of the order 10^5 yr, if the sedimentation rate was about 1-2 cm/10^3 yr.

The amount of secondary Ir is too large to be runoff from land, although New Zealand was conterminous with Australia and Antarctica. It is difficult to judge the contribution of these two continents, but this is likely to be minimal because Woodside Creek was in a purely marine environment at a depth

of 600 to 800 m. More likely secondary Ir is fallout eroded from elevated
sea-floor sites that was redeposited in topographic lows. Such topographic
lows have the best chance of retaining their primary fallout, but at the price
of becoming sinks for secondary fallout. Thinning or disappearance of
boundary clay on the walls of depressions has actually been seen at Stevns
Klint, Denmark (29).

Elemental carbon shows an even greater tendency to concentrate in the
secondary fallout (Fig. 2). Log (C_{elem}/Ir) rises steadily in the 3 layers of
the boundary clay (4.6,4.8,5.2), levels off at 5.7 ± 0.1 in the next 7
intervals, where the curves run roughly parallel, and then rises to 6.2 ± 0.3
before declining again above +213 cm. The soot/Ir ratio, on the other hand,
tends to fluctuate around the boundary clay value, though with occasional,
large deviations reflecting in part errors in the soot estimates (12). A
possible explanation of the soot-Ir correlation is that the soot and Ir-
bearing ejecta became tightly associated, perhaps by mutual coagulation in the
stratosphere (silicate and carbon particles tend to become oppositely charged,
and thus attract each other). Without such coagulation, there would have been
strong size sorting of soot and silicate ejecta, as soot, with a median radius
of 0.11 μm (1), should have taken 10^2-10^4x longer to settle. On the other
hand, the coarse carbon, with a lower charge/mass ratio, may have been less
strongly bound to the ejecta, thus becoming fractionated from Ir in both
primary and secondary fallout. But since carbon, unlike Ir, has plausible
terrestrial sources, we must keep in mind the possibility that some of it --
e.g. the peak at +28 cm -- was produced by later, local fires. We shall
return to this question in a later section.

<u>Carbon and Oxygen Isotopes: Carbonate.</u> The $\delta^{13}C$ value abruptly becomes

1.3% lighter in the first 0.3 cm of the boundary clay (Fig. 5), but then

returns almost to upper Cretaceous values in the next 0.3 cm. Such brief

excursions in carbonate $\delta^{13}C$ have been seen at most other marine K-T boundary

sites (30,31). They are generally attributed to a sharp drop in

bioproductivity that disrupted the preferential conversion of ^{12}C carbonate

species to organic matter, thus causing newly precipitated carbonate to be

light (32). Possibly even more important may have been influx of light CO_2

from land (33), as 0.013 g/cm² of soot should have been accompanied by ~1

g/cm² of CO_2. The maximum excursion is confined to the bottom part of the

clay [as at the only other site -- Caravaca, Spain -- that was studied at high

resolution (34)], and hence can have lasted only a short time (months?). The

return to Cretaceous values was very rapid, except for a minor bulge at 1-5

cm. It is not yet possible to resolve the factors that may have been

responsible: recovery of bioproductivity or mixing with deeper waters

containing heavier CO_3^-.

The $\delta^{18}O$ values (Fig. 5) also show a sharp swing to lighter values in the

first 0.3 cm, but then briefly return to Cretaceous values in the next 0.1 cm

(confirmed by triplicate measurements) before turning lighter again in the

next 0.2 cm. Above the boundary, the data trace out a distinct trend to +35

cm, with a maximum at 5.8-9.3 cm. This trend appears to be real, judging from

its smoothness and large amplitude (compared to the experimental precision of

± 0.1%). Curiously, the oxygen data -- in contrast with the carbon data --

never return to Late Cretaceous values, remaining about 1.5 or 2% lighter even

at +168 cm.

The oxygen isotope ratios in carbonate are a function not only of

temperature but also of salinity, biological species, degree of

disequilibrium, etc. If these other factors are neglected, then the data would seem to imply a brief ~10° rise followed by a ~5° drop and another ~5° rise, all within the short time interval represented by the boundary clay. The latter apparent warming -- in spite of some fluctuations -- persisted to at least +168 cm, which suggests that the changes in the oceans around New Zealand were permanent. The high paleolatitude of the S. Island of New Zealand (60° S.) and similar data from DSDP 524 (32) might possibly suggest changes in the circulation patterns of the southern oceans, though clearly more data are needed. In contrast, the trends observed in N. Hemisphere sites (e.g. 31,32,34) show either a period of cooling or no change in surface water temperature.

Carbon Isotopes: Elemental Carbon. Fig. 6 shows carbon isotope data for total and elemental carbon as well as kerogen, which was determined by difference and therefore has larger errors.

The elemental carbon from -4.5 to +168 cm is remarkably constant and is about 1‰ heavier than its counterpart in the Cretaceous (-25.35 ± 0.26‰ vs -26.48 and -26.16‰; 35). This supports our earlier conclusion that all this carbon is fallout from a single source. Moreover, there seems to be little isotopic difference between soot and coarse carbon, as samples differing widely in soot content have virtually identical isotopic compositions (for example, the intervals 0-0.3 cm and 5.8-9.3 cm, with 91% and 1% soot, have $\delta^{13}C$ = -25.17 and -25.12‰).

Carbon Isotopes: Kerogen. Cretaceous kerogen values are sparse and of variable accuracy (Fig. 6), as the total carbon content is low and the elemental carbon content even lower, often too little for isotopic measurement. We shall therefore ignore the variations in the Tertiary, which

are comparable to those in the Cretaceous, and confine ourselves to the large variations in the boundary clay: a 3‰ swing to lighter values followed by a 7‰ rebound to heavier values.

The 3‰ swing to -29‰ (Fig. 6) at 0-0.3 cm resembles that at +27 cm and thus may have the same commonplace cause, though it occurs over a far shorter depth interval and especially time interval (<0.1 yr). However, a more interesting possibility in terms of the impact theory is that this was live plankton that had become isotopically lighter after prolonged respiration due to darkness; a shift of -6‰ has actually been seen in the laboratory after 12 days of darkness (36).

The 7‰ shift to heavier values in the next 0.1 cm, confirmed by another heavy value in the following 0.2 cm, is unprecedented in magnitude let alone speed. A possible explanation is rapid burial of dead plankton without the usual bacterial degradation. During the normal descent of dead plankton [oceanic residence time ~3 months (37,38)], the more reactive, isotopically heavy components are destroyed, leaving mainly the less reactive light components, lipids and cellulose. But the massive amounts of K-T ejecta (2-5 g/cm^2) settling rapidly through the water column would sweep along fresh plankton and other particulate organic carbon, thus protecting it from bacterial attack first by rapid descent and then by burial. The total amount of kerogen in the boundary clay, 0.0057 g C/cm^2, is comparable to the global average of POC (living and dead) in the present oceans, 0.0014 g/cm^2 (38,39), despite the fact that the latter applies to average oceanic depths and latitudes. Under normal deposition conditions, the kerogen content of sediments is only a very small fraction of the original POC flux (F_{POC}) that has survived oxidation and biodegradation. Comparison of the boundary clay

(F_{POC}~1) with normal sediments (F_{POC}~10^{-4}) suggests that considerable

differences in kerogen chemistry should exist. For instance, a prediction of

this model is that kerogen in the 0.3-0.4 cm layer of the boundary clay should

be enriched in N from amino acids, provided that they have not decomposed in

the subsequent 65 Myr.

Biomass or Fossil Carbon? No decisive test is yet available for choosing

between these two potential sources of K-T carbon (1). A high potassium

content is diagnostic of wood soot (40), but we found that the potassium in

wood soot is readily leached by the acids used to dissolve the sediment,

dropping from 24,000 to 0.3 ppm after 12 hrs at 65°C. Morphology is equally

uninformative. Griffin and Goldberg (41) have shown that carbon particles

from man-made fires can be distinguished by their shape: oil yields spheres,

wood yields elongated particles (of axial ratio generally >3:1), and coal

yields both. The K-T carbon particles (Fig. 1b) include no spheres, which

would seem to rule out oil and coal, but though most of them are elongated,

their axial ratio is less than 2:1 (mean 1.5 ± 0.2), which would seem to rule

out wood. However, the K-T particles are much smaller than those studied by

Griffin and Goldberg (~10 μm vs >38 μm but typically ~100 μm), and as they

come from a natural rather than man-made fire, it is not clear that these

morphological criteria are applicable.

Mass balance considerations show that both sources are in some trouble.

Elemental carbon abundances determined by our new procedure average 0.013 ±

0.007 g/cm² at 5 K-T boundary sites (Table 2), compared to our earlier value

of 0.021 (1). We can reconsider possible sources on the basis of this new

figure (Table 3). The meteorite itself is grossly inadequate [apart from

being ruled out by its isotopic composition: $\delta^{13}C$ = -15‰ for C1 or C2

chondrites ($\underline{43}$) vs -25.4‰ for K-T carbon]. Biomass requires very efficient conversion to soot: 7% for the present above-ground biomass and ≥2% for the Cretaceous biomass (estimated for the extreme case that the entire land area was covered with tropical rain forest). The latter value is about the same as the highest soot yield (2%) observed in forest fires. Actually, soot yields may be even higher in large fires where the oxygen supply is limited, but this factor is offset by the difficulty of burning down <u>all</u> Earth's forests. Natural fire breaks will protect some areas, and natural moisture will protect others. A higher partial pressure of oxygen -- as little as 24 vol.%, compared to the 30% inferred for the Late Cretaceous ($\underline{44}$) -- would enable even moist wood to ignite ($\underline{45}$), but would be too much of a good thing: with daily thunderstorms (present frequency is -10^4/day), wildfires would be raging all the time, burning down forests as fast as they grew.

Perhaps the most likely possibility is that trees were killed and dried by the impact, both by the prompt heating of the atmosphere and strong winds "capable of flattening forests out to a distance of 500-1000 km" ($\underline{46}$), and subsequent heating by the ejecta plume and hot fallout. The kinetic energy of the projectile, 10^{31} ergs, corresponds to 4.7 x 10^4 cal/cm^2, and even a small fraction of this would suffice to cause global wildfires.

Fossil carbon avoids the ignition problem, as it is readily flammable, yet if buried would not ignite unless exposed to air by an impact or other catastrophic event. At first glance, the supply of fossil carbon seems inadequate (Table 3) as even a 300 km crater [such as the Amirante Basin ($\underline{47}$) in <u>average</u> terrain would require that no less than 4% of the carbon be converted to soot. But the potential reservoir is very large, and so two obvious solutions are available: either terrain of above-average fossil

carbon content, or ignition of shallow carbon deposits beyond the crater rim (coal, oil, oil shales). Such ignition -- by hot fallout and infrared radiation from the ejecta plume -- could occur at distances up to 1500 km or more (48).

Cisowski and Fuller (49) have pointed out that the very abundant Cretaceous black shales are a plausible source of soot, as they ignite spontaneously in air and have been burning, off and on, ever since the Cretaceous. To explain the K-T soot layer, the fire must coincide with the impact so that soot and Ir fall out together (Fig. 2), and it must be large enough to contribute 7×10^{16} g of soot and to dominate over the background of smaller fires for at least 3 m of sediment (Fig. 2). This possibility must be studied in more detail, to see whether the required size, rarity, and coincidence with the impact are plausible.

A further clue comes from the isotopic data: elemental carbon from all 5 K-T sites examined thus far has virtually constant isotopic composition, -25.4 ± 0.3‰ (Table 2). Apparently K-T carbon comes either from a single, globally uniform source or from several local but fortuitously similar sources. Let us examine the distributions of $\delta^{13}C$ for 5 potential sources (Fig. 7): land plants and natural charcoal (representing the carbonized fraction of trees, the most relevant part of land biomass) and coal, oil, and marine sediments (which include oil shales). The interval -25 to -26‰ where K-T carbon lies is indicated by shaded bars, and the percentage of data in this interval is shown alongside the bars.

The strongest conclusion that can be drawn from Fig. 7 is that the carbon at each K-T site did not come from a separate, local source. The probability that 5 independent samples all come from the same -25 to -26‰ interval is only

0.015 for charcoal and $<2 \times 10^{-4}$ for all others. But the argument becomes less compelling as the number of sources decreases. For example, for two sources (one in Europe, one in New Zealand) the probability is small only for oil (0.0014) but is appreciable for the others, ranging from 0.024 for land plants to 0.18 for charcoal. [The biomass sources would have to be quite extended, but since the mean of at least the charcoal distribution is virtually identical to the K-T mean -- -25.2 vs -25.4‰ -- the agreement would actually improve as the sampling area got larger. The probabilities are larger still for a single source, with even oil reaching 0.038.

The most likely explanation of Table 2 thus is a single global K-T carbon component, either from a single source (fossil carbon) or from several sources but mixed globally before deposition (forests). Fossil carbon has the advantage of copious supply and ready flammability, but forests have the right average carbon isotope composition. The question remains open.

Regardless of the source, it is apparent that a global fire producing 7×10^{16} g of soot would aggravate most of the environmental stresses of an impact (2). As soot absorbs sunlight more effectively and settles more slowly than does rock dust, the darkness and cold would last longer. Poisons such as NO and NO_2 (51) would be accompanied by CO (~70 ppm) and organic pyrotoxins. The latter, in particular, may help explain the selectivity of extinction patterns, which some authors (e.g. 52,53) have claimed to be inconsistent with the non-specific stresses of an impact, as different species often have very different tolerances for chemical toxins. Lastly, the CO_2 accompanying the soot (~700 ppm) would increase the greenhouse effect due to water vapor (~8°C; 46) by another ~7°C.

Events at the K-T Boundary. Evidently K-T boundary clay contains a

record of the impact and its aftermath, which is still preserved at undisturbed sites such as Woodside Creek. Our data suggest the following sequence of events in the 3 layers studied.

0-0.3 cm. Abrupt increase in Ir concentration by a factor of 1400 over the Cretaceous, due to meteorite impact and prompt settling of ejecta. Concurrent increases in elemental carbon (210x) and soot (>7000x), due to major fires triggered by the impact. Kerogen increases by >15x, presumably due to partial sweepout of live plankton near surface and dead organic matter at depth. Carbonate content drops from 44 to 5%. The following isotopic changes occur, presumably due to the processes indicated. a. Carbonate $\delta^{13}C$ becomes 1.3‰ lighter (decreased bioproductivity). b. Carbonate $\delta^{18}O$ becomes 1.8‰ lighter (temperature increase by ~10°C). c. Kerogen $\delta^{13}C$ becomes 3‰ lighter (darkness or selective precipitation of dissolved organic matter).

0.3-0.4 cm. Abundances decline relative to the basal layer: Ir (0.35), elemental carbon (0.50), soot (0.40), kerogen (0.45), carbonate (0.67)(54). Carbonate $\delta^{13}C$ becomes slightly heavier by 0.9‰; $\delta^{18}O$ by 1.3‰ (±0.5‰), and kerogen $\delta^{13}C$ becomes 7‰ heavier (rapid burial without biodegradation).

0.4-0.6 cm. Abundances continue to drop relative to the basal layer: Ir (0.14), elemental C (0.54), soot (0.22), kerogen (0.31), while carbonate increases (2.9x) and kerogen $\delta^{13}C$ remains 5‰ heavier (continued rapid burial without biodegradation).

The chemical and isotopic differences among the 3 layers show that the scale length for mixing was less than 0.1 cm in the boundary clay at this site, permitting a detailed stratigraphic record to survive. The data thus far suggest a series of environmental changes remarkably like those expected from a meteorite impact (2) followed by major fires (1). However, these

trends should be confirmed at high resolution at other undisturbed sites, and the interpretations -- some of which are not unique -- must be carefully scrutinized.

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11. The oxidation procedure was adapted from a procedure for removal of meteoritic kerogen [M. Tang, *Isotopically Anomalous Ne and Xe in Meteorites and their Carriers, Diamond and SiC*: Ph.D. thesis, University of Chicago, Illinois (1987); Tang *et al.*, *Geochim. Cosmochim. Acta*, in press (1988)]. The carbonaceous residues were heated for 60 hr at 50°C in 0.1 N $Na_2Cr_2O_7$-2 N H_2SO_4. Control experiments with HF,HCl-insoluble residue from Woodside Creek boundary clay showed 3 components, with the following half-lives: ≤ 5 hr (kerogen and soluble organic compounds), 71 hr (reactive elemental carbon, e.g.

the linkages between soot spherules, Fig. 1a) and 600 hr (soot and coarse carbon). First-order kinetics for the last 2 components was established by several experiments lasting up to 2500 hr, where the reaction was monitored both by loss of weight and by growth of Cr^{3+}. During the standard, 60-hr etch, loss of kerogen was essentially complete; loss of elemental C was only around 7% and could be accurately corrected for, as the 71 hr component was only a minor part of the total (~15%). Control experiments with industrial carbon black showed no isotopic fractionation after a similar degree of mass loss.

12. We measured the major and minor axes of all soot and coarse carbon particles within a known area of an SEM photograph, and computed their volumes by the method of Medalia and Heckman [A.I. Medalia and F.A. Heckman, Carbon 7, 567 (1969)] for non-spherical particles. Neglecting possible differences in density, we obtained the mass fraction of each class directly from its volume fraction. The reproducibility of the method was ±6%, if care was taken to avoid the edges of each mount, where an up to four-fold sorting by size had taken place. However, as the SEM mounts contained only ~10^{-6} g of sample, occasional larger sampling errors cannot be ruled out; they may be responsible for some of the fluctuations in the soot values in Fig. 2. Non-carbonaceous particles (such as rutile) were recognized by morphology and eliminated.

13. The Cretaceous average is not well-determined, as total C and Ir are low and variable, whereas elemental C is undetectable in some cases. Moreover, the values near the boundary are affected by mixing or diffusion. The averages cited in the text are based on the following samples: Ir = 0.076 ± 0.09 ppb (-27,-41 cm), elemental C = 22 ± 7 ppm

(-12,-27,-41,-68,-75 cm), and soot = <1 ppm (-27,-41,-68,-75 cm).

14. The 2 cm boundary clay sample plotted here actually comes from another location, about 50 m away. The depth scale for the Tertiary has therefore been raised by +2 cm.

15. The very low carbon content of the 0 to -10 and -10 to -20 cm intervals is puzzling. Essentially all this carbon (0.5 and ≤1.5 ppm) is kerogen, judging from its reaction with dichromate, and since this kerogen survived, diagenetic loss of elemental carbon is unlikely. Still, since both (marine) kerogen and (terrigenous) elemental C are underabundant by $\geq 10^2$x relative to nearby Woodside Creek (Fig. 2), the main reason may have been unfavorable deposition conditions rather than lower fluxes. Presumably deposition conditions become more favorable above the boundary (due to changes in currents or local topography?), as carbon concentrations from 0 to +37 cm are only 4 to 7x lower than at Woodside Creek.

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20. An upper limit to the deposition time -- at least on the impact scenario -- is provided by the survival of numerous animal taxa which would have died out, had the darkness lasted more than one to two years.

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35. The slight drift toward lighter values from +22 to +168 cm qualitatively suggests contributions of lighter, local material, but as the carbon levels still are 10^1-10^2x higher than in the Cretaceous (Fig. 2), it seems likely that secondary K-T fallout still dominates even in this interval.

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54. This value is based on a direct determination of %$CaCO_3$ by acid

dissolution for each sample, rather than by inference of %$CaCO_3$ from Ca abundances (as in Fig. 4).

Table 1. Integrated Ir and C Abundances
at Woodside Creek, New Zealand

	Interval	Ir	Elem. C	Soot
	cm	$\dfrac{ng}{cm^2}$	$\dfrac{mg}{cm^2}$	$\dfrac{mg}{cm^2}$
Boundary Clay,	0.0-0.6	91	4.8	3.6
Tertiary,	0.6-34	200	84	15
Tertiary,	0.6-250	470	390	16

Table 2
Elemental Carbon in K-T Boundary Clay
at 5 Sites

Site		Carbon Abund. g/cm^2	$\delta^{13}C_{PDB}$ (‰)[*]
Woodside Creek,	NZ	0.0048	-25.23
Chancet Rocks,	NZ	0.025	-25.42
Stevns Klint,	DK	0.011	-25.81
Caravaca,	E	0.010	-25.00
Gubbio,	I	0.013	-25.48
	Mean:	0.013 ±0.007	-25.39 ±0.30

[*]All errors ± 0.05‰.

Table 3. Sources of Elemental Carbon
at the K-T Boundary

Source	Global Carbon Abund. g/cm²	Implied Soot Yield %
K-T carbon, ave. 5 sites	0.013	--
Meteorite (C1)	0.007	200
Biomass, present	0.2	7*
Biomass, pre-civil.	0.5	3*
Biomass, Cretaceous	≤0.8	≥2*
Fossil carbon	2300	17-4†

*Range for forest fires: 0.1-2% (42).

†For 150-300 km crater in average terrain, with 2300 g/cm² of fossil carbon.

Figure Captions

1. Soot of characteristic "grape bunch" morphology dominates in boundary clay (1a, 0.3-0.4 cm above boundary), whereas irregularly shaped, platy or pitted coarse carbon dominates at higher levels (1b; 17.4-19.9 cm and 3.6-5.8 cm). All samples were etched with dichromate to remove kerogen.

2. Iridium, elemental C, and especially soot rise steeply at the K-T boundary, by factors of 1400, 210, and >7000. Soot appears in the first 0.3 cm interval, showing that fires started before the fallout had settled. After an initial drop above the boundary, all 3 decline gradually, returning to Cretaceous levels only at ~250 cm. This delayed fallout appears to be secondary, redeposited by lateral transport in topographic lows. Soot is the major form of elemental C in the basal layer of the boundary clay, but becomes less abundant at higher levels. Vertical bars indicate depth range of discontinuous samples.

3. At Chancet Rocks, N.Z., both Ir and elemental C show their characteristic rise at the K-T boundary, by factors of 290 and 3×10^5.

4. In the interval -4.5 to 0 cm, meteoritic Ir rises, but so do non-meteoritic Fe, Al, and Sb -- all good indicators of boundary clay -- while the carbonate content drops. Apparently the rise in Ir represents admixture of ~5% boundary clay to the 0 to -4.5 cm sample, not a premonitory Ir signal.

5. Carbon becomes isotopically lighter by -1.3‰ in the basal 0.3 cm of the boundary clay, due to decreased bioproductivity, addition of light CO_2 from fires on land, or both.

Oxygen shows larger and more complex fluctuations, which may reflect variations in temperature, biological species, salinity, or degree of disequilibrium. If they were due solely to temperature, then they would imply

a ~10° rise followed by a ~5° drop and another ~5° rise, all within the short time interval represented by the boundary clay. The light $\delta^{18}O$ values persist to at least +168 cm, suggesting a permanent warming of the oceans around New Zealand. The +0.35 cm sample has a low $CO_3^=$/kerogen ratio, which may cause contamination of the CO_2 extracted for analysis. Individual analyses are shown for this sample (open circles) in addition to the average value (closed circle). Repeat analyses on the other two boundary clay samples (+0.15 and +0.50 cm), which have slightly higher $CO_3^=$/kerogen ratios, were within analytical error.

6. Elemental C from -4.5 to +168 cm has nearly constant $\delta^{13}C$, supporting the earlier interpretation of this carbon as fallout from a single source. Total carbon shows larger variations -- especially in the boundary clay -- which must be inherent in the kerogen. The shift to -29‰ at 0-0.3 cm may be due to respiration in darkness (which preferentially eliminates ^{13}C), and the subsequent shift to -22‰ may reflect rapid sweepout and burial of particulate organic carbon, without the usual bacterial degradation that preferentially consumes isotopically heavy proteins and carbohydrates. FR: a 164 g sample of Cretaceous limestone from the nearby Flaxbourne River site.

7. Isotopic composition of K-T carbon (shaded bars) falls within range of all potential reservoirs [data adapted from (50)]. However, fraction of samples between -25 and -26‰ is small except for charcoal, and thus multiple sources -- one for each site in Table 2, or even 2-3 regional sources -- are improbable. Only for charcoal (representing trees) are multiple sources tenable, as the mean of the distribution virtually coincides with the mean for K-T carbon.
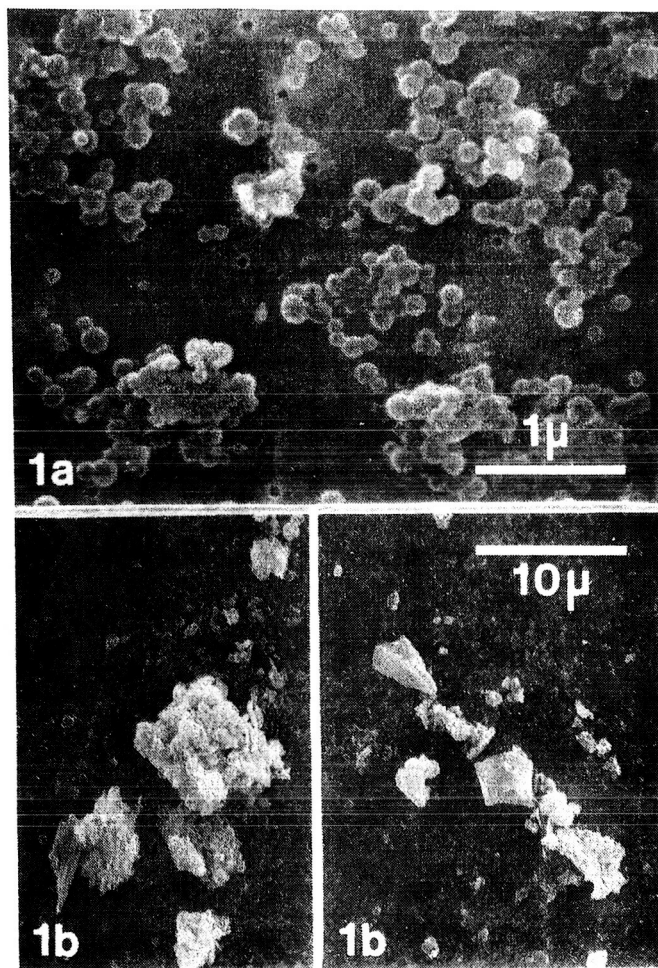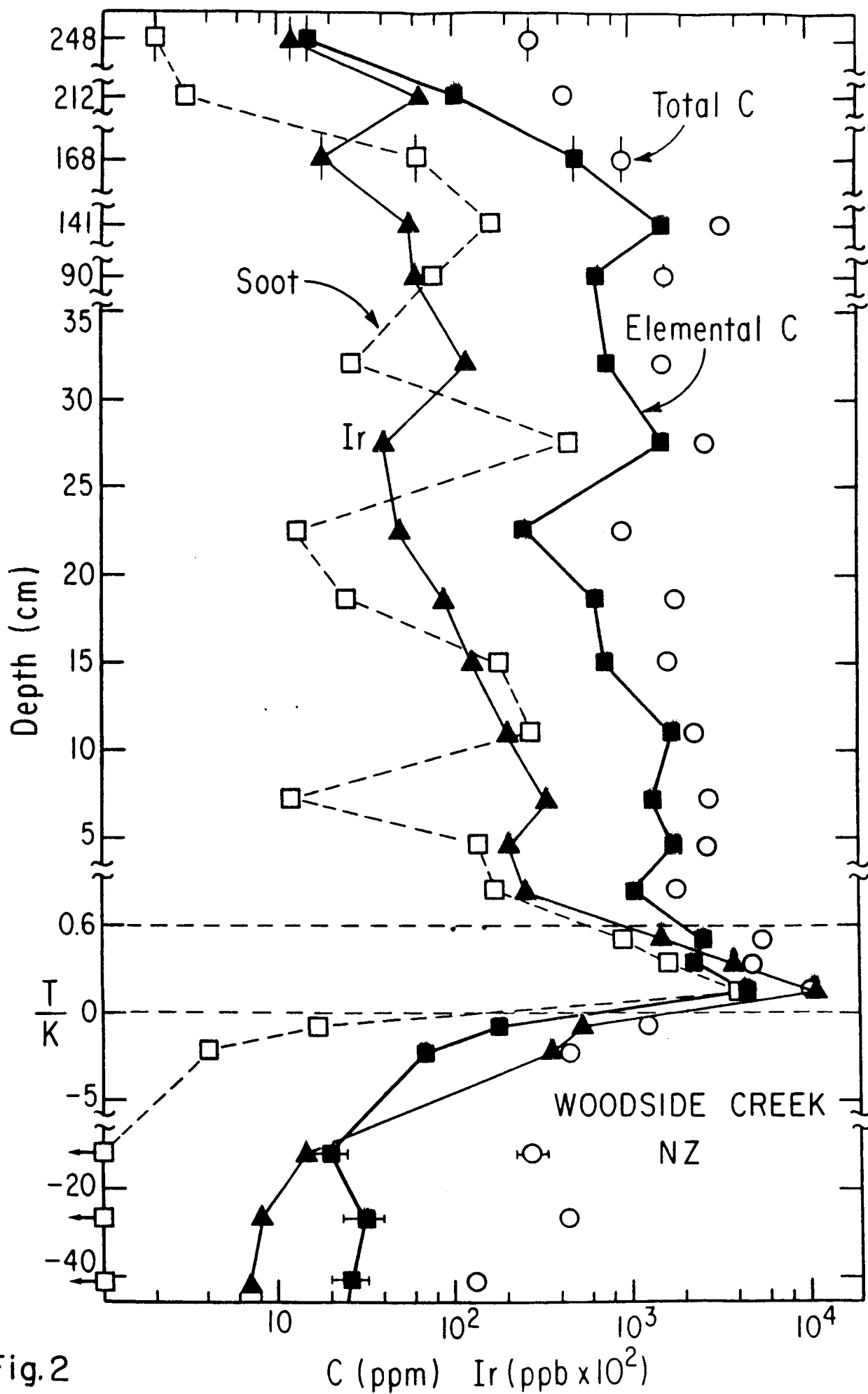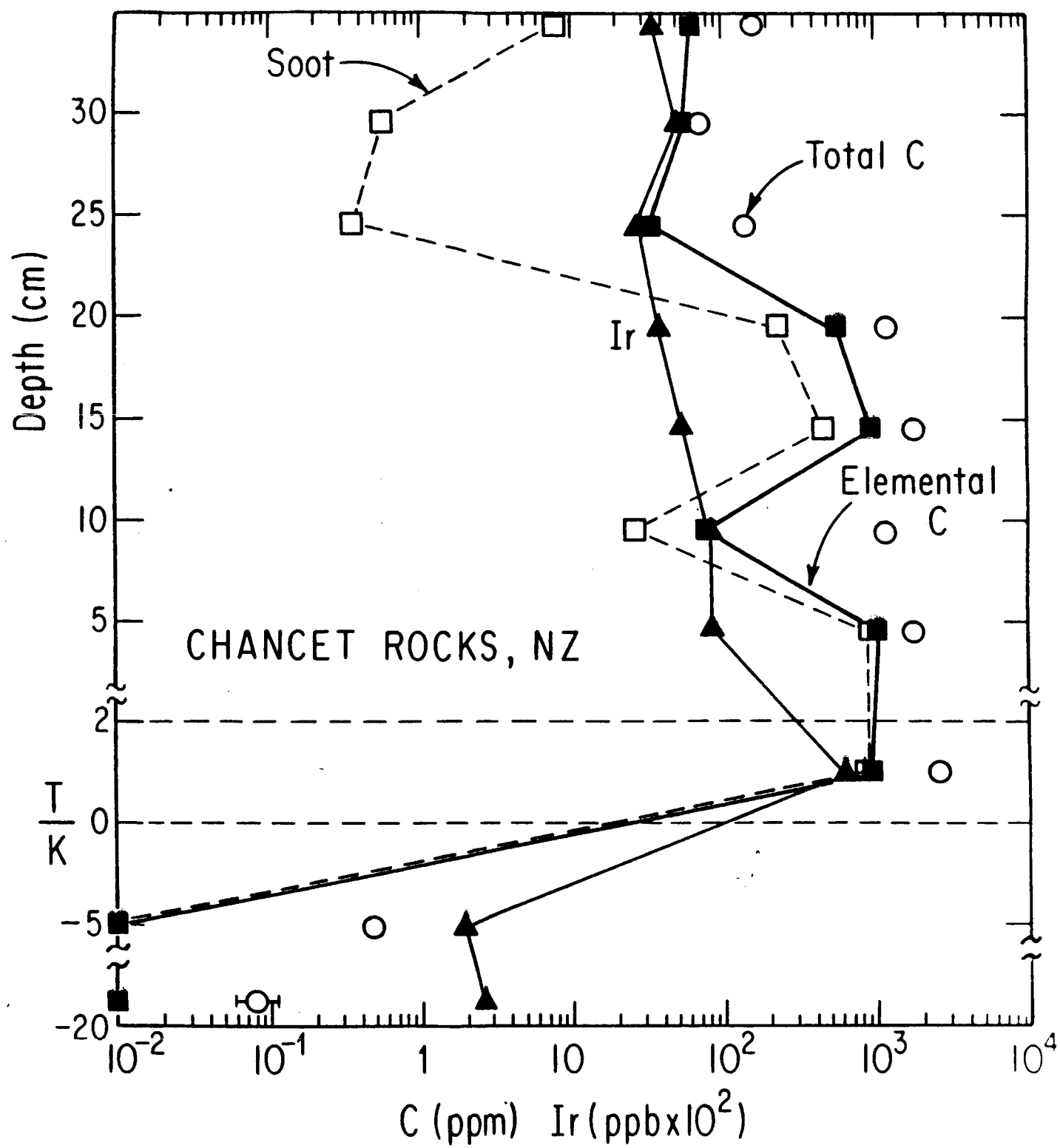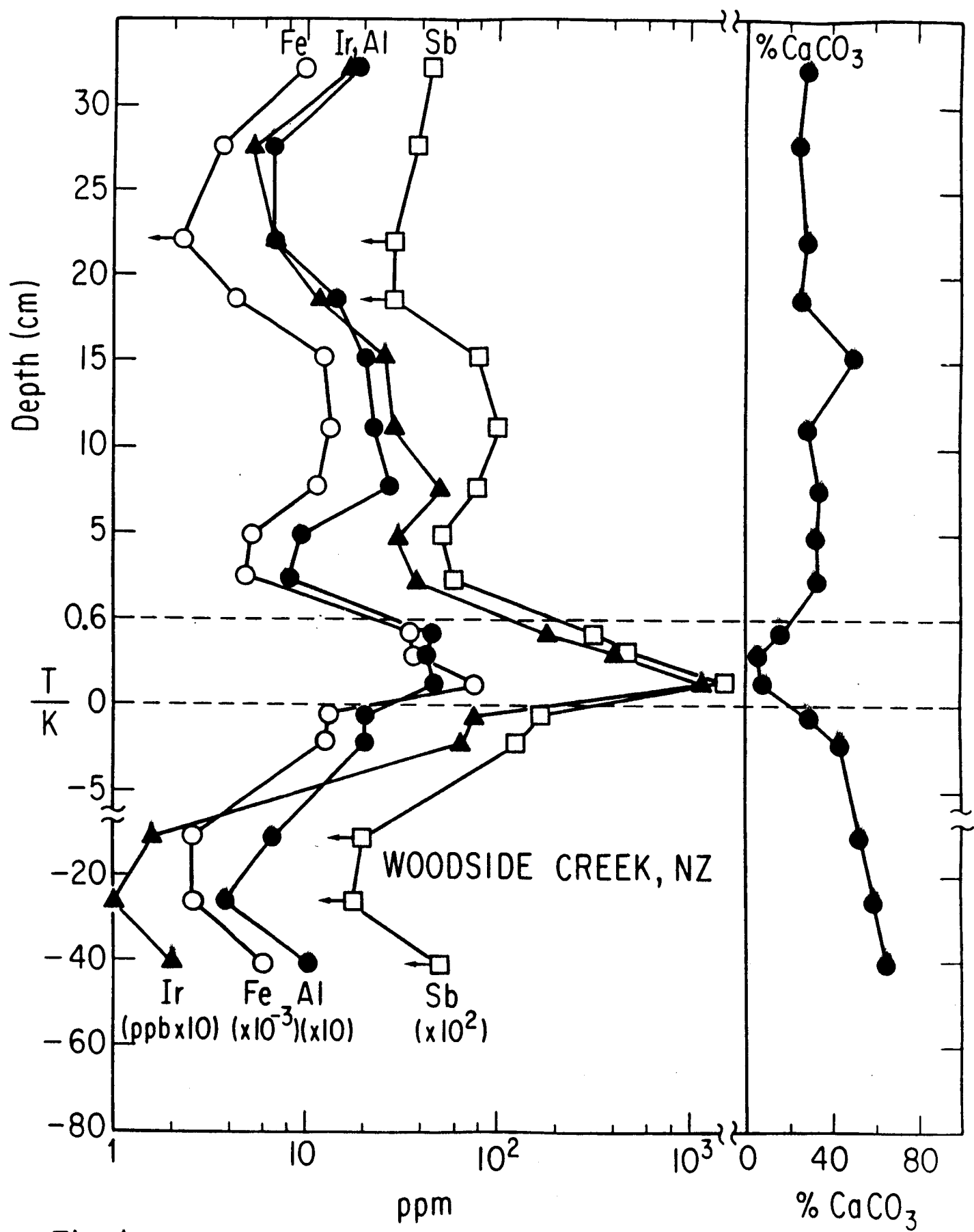
1a

1μ

1b

10μ

1b

Fig. 1

Fig. 2

Fig.3

Fig.4

Fig.5

δ¹³C δ¹⁸O

$\delta^{13}C$ $\delta^{18}O$

CARBONATE
WOODSIDE CREEK, NZ

±0.1‰   ±0.1‰

$\delta^{13}C_{PDB}$ (‰) $\delta^{18}O_{PDB}$ (‰)

Depth (cm)

248
212
168
141
90
35
30
25
20
15
10
5
0.6
T/K
0
-5
-20
-40
-60
-80

+1 +2   -5 -4 -3

Fig.6

Fig.7